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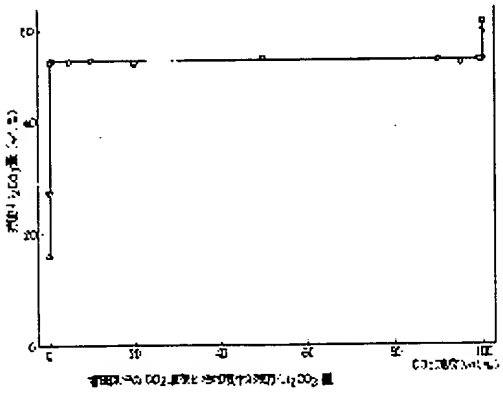
(54) MANUFACTURE OF POSITIVE ELECTRODE MATERIAL

(57)Abstract:
PURPOSE: To adjust a residual amount of lithium carbonate by synthesizing a material at least partly in the atmosphere of specific concentration of CO2 gas, in the case of synthesizing the positive electrode material mainly composed of specific lithium compound oxide to contain lithium carbonate.
CONSTITUTION: In the case of synthesizing a positive electrode material mainly composed of lithium compound oxide, represented by a general formula LixMO2 (where, M shows a transition metal of one kind or more and X is $0.05 \leq X \leq .10$), and formed by containing lithium carbonate, synthesizing is performed at least partly in the atmosphere with CO2 concentration 0.1vol.% or more and less than 100vol.%. In this way, a residual amount of lithium carbonate in the positive electrode material is increased, further when the CO2 gas concentration is increased, the residual amount of lithium carbonate is fixed, and accurate control can be performed. Accordingly, a desired effect of internal pressure rise of a battery is provided in the positive electrode material, and safety of the nonaqueous electrolyte secondary battery of explosionproof closed structure can be improved.



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CLAIMS

[Claim(s)]
[Claim 1] The lithium multiple oxide expressed with a general formula Lix MO2 (however, M expresses one or more sorts of transition metals, and is 0.05<=X<=1.10) is made into a subject, and it faces compounding the positive-electrode ingredient which comes to contain a lithium carbonate, and is CO2 in a part of at least composition. The manufacture approach of a positive-electrode ingredient that concentration is characterized by carrying out in the ambient atmosphere of under 100 capacity % more than 0.1 capacity %.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of the positive-electrode ingredient used in the nonaqueous electrolyte rechargeable battery equipped with the current interrupting device.
[0002]
[Description of the Prior Art] In recent years, by advance of an electronic technique, high-performance-izing of electronic equipment, a miniaturization, and portable-ization progress, and the demand of the rechargeable battery of the high energy consistency used for these electronic equipment has become strong. Conventionally, as a rechargeable battery used for these electronic equipment, although a nickel cadmium battery, a lead cell, etc. are mentioned, it is still inadequate in that discharge potential obtains a low cell with high energy density by these cells.
[0003] Recently, research and development of the nonaqueous electrolyte rechargeable battery which uses the matter in which a dope and a dedope of a lithium ion like a carbon material are possible as a negative electrode for a lithium or a lithium alloy pan, and uses lithium multiple oxides, such as a lithium cobalt multiple oxide, for a positive electrode are performed briskly. Cell voltage is high, this cell has a high energy consistency, and there is also little self-discharge, and it is a cell excellent in the cycle property.
[0004] However, if the current of quantity of electricity more than predetermined flows by a certain cause at the time of charge and the above nonaqueous electrolyte rechargeable batteries will be in a overcharge condition, cell voltage becomes high, the electrolytic solution etc. will decompose, gas will occur, and cell internal pressure and cell temperature will rise. Furthermore, if this overcharge condition continues, an anomalous reaction called rapid disassembly of an electrolyte or an active material occurs, and the faulted condition of generation of heat and the comparatively rapid breakage accompanied by a temperature rise may be presented.
[0005] As a cure about this problem, this invention persons had the current interrupting device which operates according to the rise of cell internal pressure, and proposed the cell using the lithium multiple oxide (LiX MO2) with which the front face was covered with

the lithium carbonate (Li2 CO3) which serves as a cell internal pressure rise agent as a positive-electrode ingredient. By this cell, if a overcharge condition progresses, for example, the lithium carbonate in a positive electrode will be disassembled electrochemically, carbon dioxide gas will occur, cell internal pressure rises by this generation of gas, a current interrupting device operates, and the charging current is intercepted. Therefore, advance of the anomalous reaction inside the cell in overcharge stops, and prevention of generation of heat accompanied by the rapid temperature rise of a cell and comparatively rapid breakage is attained.

[0006] As an approach of compounding the lithium multiple oxide covered in the above-mentioned cell with the lithium carbonate used as a positive-electrode ingredient For example, measure and the carbonate and lithium carbonates of transition metals, such as cobalt and nickel, are calcinated so that Li/M (mole ratio) may become larger than X. While generating a lithium multiple oxide, the lithium multiple oxide is compounded beforehand and there are an approach of making a lithium carbonate remaining, and a method of adding and carrying out remelting of the lithium carbonate to this lithium multiple oxide.

[0007]

[Problem(s) to be Solved by the Invention] However, when a positive-electrode ingredient is compounded by the above-mentioned approach, the amount of lithium carbonates which remains in a positive-electrode ingredient cannot control the amount of lithium carbonates which remains the circumference of the bottom to Haruka rather than the amount of theoretical values. For this reason, it is difficult to give the desired cell internal pressure rise effectiveness to a positive-electrode ingredient.

[0008] Then, this invention is proposed in view of such the conventional actual condition, and a lot of lithium carbonates can be made to remain in a positive-electrode ingredient, and it aims at offering the manufacture approach of the positive-electrode ingredient which can control the amount of residual lithium carbonates.

[0009]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of this invention persons' repeating examination wholeheartedly, the amount of lithium carbonates which remains in a positive-electrode ingredient is CO2 to a synthetic ambient atmosphere. By making it exist, it increases and came to find out becoming controllable.

[0010] The manufacture approach of the positive-electrode ingredient of this invention is completed based on such knowledge. General formula Lix MO2 (however, M expresses one or more sorts of transition metals) 0.05<=X<=1.10 -- it is -- the positive-electrode ingredient which makes a subject the lithium multiple oxide expressed and comes to contain a lithium carbonate -- compounding -- facing -- a part of at least composition -- CO2 Concentration is characterized by carrying out in the ambient atmosphere of under 100 capacity % more than 0.1 capacity %.

[0011] The positive-electrode ingredient manufactured in the manufacture approach of this invention makes a subject the lithium multiple oxide used as positive active material, and comes to contain the lithium carbonate used as a cell internal pressure rise agent. As the above-mentioned lithium multiple oxide, the lithium multiple oxide 2 shown by LiX MO2 (however, M expresses one or more sorts of transition metals, and is 0.05<=X<=1.10), for example, LiCoO, LiNiO2, LiX NiY Co (1-Y) O2, etc. are

mentioned (however, 0.05 <=X1.10, 0< Y<1).
[0012] The positive-electrode ingredient which consists of such a lithium multiple oxide and a lithium carbonate For example, the carbonate and lithium carbonates (Li2 CO3) of transition metals (M), such as cobalt and nickel How to make a lithium carbonate remain while measuring, mixing so that Li/M (mole ratio) may become larger than X, calcinating in a 600 degrees C - 1000 degrees C temperature requirement and generating a lithium multiple oxide, Or the lithium multiple oxide is compounded beforehand and it can compound by the approach of adding and remelting a lithium carbonate in this lithium multiple oxide etc. Moreover, even if it uses a hydroxide and an oxide instead of the carbonate of transition metals in an above-mentioned approach, it is compoundable similarly.
[0013] In order to make a lot of lithium carbonates remain and to make possible control of the amount of residual lithium carbonates into a positive-electrode ingredient by this invention here, it is CO2 in a part of composition of a positive-electrode ingredient at least. Gas concentration decides to carry out in the ambient atmosphere of under 100 capacity % more than 0.1 capacity %.
[0014] That is, the amount of lithium carbonates which remains in a positive-electrode ingredient is CO2 in a synthetic ambient atmosphere. It increases by making gas exist and is CO2 in a synthetic ambient atmosphere further. By raising gas concentration, the amount of residual lithium carbonates becomes fixed, and the exact control of it is attained. In addition, CO2 in a synthetic ambient atmosphere If gas concentration is made into 100 capacity %, disassembly of a lithium multiple oxide will take place and the function as a positive-electrode ingredient will deteriorate. Therefore, while aiming at increase of the amount of residual lithium carbonates, in order to maintain the function of a positive-electrode ingredient in this invention, it is CO2 in a synthetic ambient atmosphere. Gas concentration is made under into 100 capacity % more than 0.1 capacity %.
[0015]
[Function] A lithium multiple oxide is made into a subject, and it faces compounding the positive-electrode ingredient which comes to contain a lithium carbonate, and is CO2 about composition. When it carries out in the air which is not adjusting gas concentration, the amount of lithium carbonates which remains in a positive-electrode ingredient cannot become lower to Haruka than a theoretical value, and the amount of lithium carbonates which remains cannot be controlled.
[0016] On the other hand, it is CO2 in a part of composition [at least] of the above-mentioned positive-electrode ingredient. When it carries out in the ambient atmosphere by which gas concentration was made the predetermined density range, the amount of residual lithium carbonates in a positive-electrode ingredient increases, and it is CO2 in a synthetic ambient atmosphere further. If gas concentration is raised, the amount of residual lithium carbonates will become fixed, and the exact control of it will be attained. This is considered to be based on the following reasons.
[0017] That is, it is CO2 about composition of a positive-electrode ingredient. In carrying out in the air which is not adjusting gas concentration, as shown in ** 1, on the occasion of high temperature processing, such as baking and remelting, the decomposition reaction (it sets to ** 1 and is a rightward reaction) of a lithium carbonate advances.
[0018]

[Formula 1]

$$Li_2CO_3 \rightleftarrows Li_2O + CO_2\uparrow$$

[0019] On the other hand, it is CO2 about composition. When gas concentration carries out in the ambient atmosphere of a predetermined density range, the decomposition reaction of the lithium carbonate which faces high temperature processing is suppressed. Moreover, lithium oxide which is a decomposition product even if a lithium carbonate decomposes and CO2 made to exist in a synthetic ambient atmosphere Gas reacts and a lithium carbonate is compounded. Therefore, increase of the amount of residual lithium carbonates in a positive-electrode ingredient will be attained.

[0020]

[Example] The suitable example of this invention is explained based on an experimental result.

[0021] CO2 after measuring and mixing example 1 lithium carbonate and cobalt carbonate so that it may be set to Li/Co(mole ratio) =1.15 In the oxygen existence ambient atmosphere of concentration 0.2 capacity %, it calcinated for 24 hours and 900 degrees C (sample sample 1) of positive-electrode ingredients were compounded.

[0022] CO2 in an example 2 - example 11 firing environments The positive-electrode ingredient (the sample sample 2 - sample sample 11) was compounded like the example 1 except having changed concentration, as shown in Table 1.

[0023] After measuring, mixing so that it may be set to Li/Co(mole ratio) =1.15 and calcinating example 12 lithium carbonate and 900 degrees C of cobalt carbonate in air for 12 hours, it is CO2 further. 900 degrees C (sample sample 12) of positive-electrode ingredients were compounded by calcinating for 12 hours in the ambient atmosphere of concentration 5.0 capacity %.

[0024] After measuring and mixing so that it may be set to Li/Co(mole ratio) =1.15, example of comparison 1 lithium carbonate and 900 degrees C of cobalt carbonate were calcinated in air for 24 hours, and the positive-electrode ingredient (comparison sample 1) was compounded.

[0025] CO2 in example of comparison 2 firing environments The positive-electrode ingredient (comparison sample 2) was compounded like the example 1 except having made concentration into 100 capacity %.

[0026] About each positive-electrode ingredient compounded by carrying out such, when an X diffraction is performed, the comparison sample 2 is removed, and it is LiCoO2. Composition can be checked, and it also sets into which positive-electrode ingredient, and is Li2 CO3. The diffraction peak existed.

[0027] Next, the amount of lithium carbonates which remains in each positive-electrode ingredient was investigated. The result is shown in Table 1 and drawing 1 . In addition, the amount of lithium carbonates in a positive-electrode ingredient is CO2 which decomposed and generated the sample with the sulfuric acid. It is CO2 by introducing into the solution containing barium chloride and a sodium hydroxide, making it absorb, and titrating this solution with a hydrochloric-acid standard solution. The quantum of the concentration was carried out and it converted from this quantum value.

[0028]

[Table 1]

	合成雰囲気中の CO_2 濃度（容量%）	正極材料中の残存炭酸リチウム濃度（重量%）
サンプル試料 1	0.2	2.72
サンプル試料 2	0.5	5.31
サンプル試料 3	1.0	5.34
サンプル試料 4	5.0	5.32
サンプル試料 5	10.0	5.36
サンプル試料 6	20.0	5.33
サンプル試料 7	50.0	5.40
サンプル試料 8	90.0	5.36
サンプル試料 9	95.0	5.32
サンプル試料10	99.0	5.36
サンプル試料11	99.9	5.35
サンプル試料12	空気中で12時間焼成した後、CO_2 濃度5.0容量%雰囲気中で12時間焼成	5.34
比較試料 1	0	1.60
比較試料 2	100.0	13.41

[0029] The amount of lithium carbonates which remains in a positive-electrode ingredient from drawing 1 and Table 1 is CO2 in a synthetic ambient atmosphere. It increases by making gas contain and is CO2. By carrying out concentration more than 0.5 capacity % shows becoming fixed. It is CO2 in [from this] a positive-electrode ingredient. When increasing the amount of residual lithium carbonates, it is effective, and it is CO2 in a synthetic ambient atmosphere especially to make gas contain. It turned out that more than 0.5 capacity %, then the amount of residual lithium carbonates become fixed, and the exact control of the amount of residual lithium carbonates of them is attained in concentration.

[0030] However, it is CO2 in a synthetic ambient atmosphere so that the X diffraction result of the comparison sample 2 may show. LiCoO2 which is positive active material when concentration is made into 100 capacity % Decomposition takes place. Therefore, in order to maintain the function of a positive-electrode ingredient, it is CO2 in a synthetic ambient atmosphere. Gas concentration was understood that to consider as less

than 100% is required.
[0031] In addition, in this example, although a lithium carbonate and cobalt carbonate were used as a start raw material, it was checked that the effectiveness same also as starting material is acquired in an oxide, a hydroxide, etc. instead of cobalt carbonate. Moreover, it is LiCoO2 also as positive active material to compound. Lithium multiple oxide of an except (for example, even when LiX NiY Co (1-Y) O2 (however, 0.05<=X<=1.10, 0< Y<=1) was adopted, this invention demonstrated the same effectiveness.)
[0032]
[Effect of the Invention] The manufacture approach of the positive-electrode ingredient of this invention makes a lithium multiple oxide a subject so that clearly also from the above explanation, and it faces compounding the positive-electrode ingredient which comes to contain a lithium carbonate, and is CO2 in composite [at least / a part of]. It is possible to increase the amount of lithium carbonates to which it remains in a positive-electrode ingredient since concentration carries out in the ambient atmosphere of under 100 capacity % more than 0.1 capacity %.
[0033] Therefore, according to this invention, it becomes possible to give the desired cell internal pressure rise effectiveness to a positive-electrode ingredient, and it becomes possible to raise more the safety of the nonaqueous electrolyte rechargeable battery of the explosion-proof sealing structure which uses the above-mentioned positive-electrode ingredient.

Drawing 1